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### (54) POLYESTER PARTICLE

#### (57)Abstract:

PURPOSE: To obtain polyester particles having a low specific gravity, a low dielectric constant, closed cells in the inside, and specified particle size, void content, etc., by converting a polyester resin having ionic groups into hollow particles by a specific method.

CONSTITUTION: The title particles mainly comprise a polyester resin contg. 20-200eq./ton ionic group and have a vol.-average particle size of 0.5-100 $\mu$ m and a void content of 1-99vol.%, each particle contg. a closed cell or cells filled with a gas or liq. The particles are produced, e.g. by dissolving the resin in a water-sol. org. compd. (e.g. ethanol) and adding water to the resulting soln. to form a W/O/W emulsion, and are suitable as a delusterant, an antiblocking agent, a carrier for chromatography, etc.

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## DETAILED DESCRIPTION

## [Detailed Description of the Invention]

[0001]

[Industrial Application] this invention relates to the polyester resin particle which has many stomata especially inside a particle about the resin particle briskly used as a flattening, blocking prevention material, \*\*\*\* for chromatographies, \*\*\*\* for medicines, powder coatings, gap adjustment material, the toner for electrophotography, an electroviscous fluid, cosmetics, etc.

[0002]

[Description of the Prior Art] The particle obtained by "polymerization granulation methods", such as an emulsion polymerization method, a suspension-polymerization method, a seed polymerization method, and a distributed polymerization method, has been used as a resin particle conventionally used for such a use. However, as for the resin particle obtained by the emulsion polymerization method and the suspension-polymerization method, the particle-diameter range is limited, and a particle size distribution will become broadcloth. Although the resin particle obtained by the seed polymerization method and the distributed polymerization method has a sharp particle size distribution, it will become very expensive. furthermore, the resin particle produced by the "polymerization granulation method", i.e., emulsion polymerization, described above, a suspension polymerization, a seed polymerization, and the distributed polymerization -- from the manufacture method -- obvious -- it is -- as -- it is limited to the resin particle of vinyl system polymer. Although the polyester system binder widely used for a paint, adhesives, etc. is excellent in the adhesive property to the high polyester film of versatility, a resin particle which replaces the particle of the above-mentioned vinyl system polymer with these to the binder of a polyester system since matching is not necessarily good was desired. This invention persons consisted of polyester resin which is condensed-system polymer, it had still more arbitrary mean particle diameters, and they had the sharp particle size distribution, and have proposed JP,3-212444,A etc. as a resin particle in which production on a industrial scale is possible. After this invention makes polyester resin contain the ionicity machine of the specified quantity and carries out micro distribution of the polyester resin at a drainage system medium, it is made to \*\*\*\*\* by controlling the underwater distributed stability of a micro dispersing element, and obtains the particle of arbitrary particle diameters and a sharp particle size distribution. This polyester particle was dissatisfied in the use of which concealment nature is required although [ unique ] it has the features, such as goodness of matching with a polyester system binder, as additives for paints, such as a flattening and blocking prevention material, etc., the use of which light-scattering nature is required, the use of which low specific gravity is required.

[0003] Conventionally, the resin particle which has a stoma inside in the use of which concealment nature, light-scattering nature, low specific gravity, adiathermancy, lightweight nature, etc. are required is used. It is the method of making the foaming agent containing and making this foaming agent foaming behind into 1 resin particle as a method of manufacturing the resin particle which has a hole such inside.

- 2) How to enclose volatile matter, such as butane, with the resin and to carry out gasification expansion

of this volatile matter behind.

3) How to make carry out melting of the resin, spray gas jet, such as air, on this, and enclose a foam.

4) How to make the matter of alkali bloating tendency contain inside a resin particle, to make an alkaline liquid permeate this resin particle, and to expand the matter of alkali bloating tendency.

\*\* is known.

[0004]

[Problem(s) to be Solved by the Invention] However, each of these methods is difficult for control of conditions etc. to manufacture efficiently certainly the resin particle which has a hole among requests difficultly. Moreover, like a general resin particle, it is the method applied mainly to the resin particle of vinyl system polymer, and it is difficult to apply to condensed-system polymer. the arbitrary mean particle diameters which the resin particle which has a hole inside according to the Prior art is restricted to vinyl system polymer as stated above, and are excellent in matching with a polyester system binder, and a sharp particle size distribution -- having -- and -- inner -- the resin particle which has a hole was not known

[0005]

[Means for Solving the Problem] That is, the polyester resin which contains an ionicity machine in the range of 20-2000eq./ton is made into a principal component, it is the range whose volume mean particle diameter  $D$  is 0.5-100 micrometers, the single or multiple independent hole filled with the gas or the liquid inside the particle exists, and this invention is a polyester particle characterized by being the range whose void content is 1 - 99vol%.

[0006] the range which it is indispensable that it is the range whose volume mean diameter  $D$  is 0.5-100 micrometers as for the particle of this invention, and is 1-50 micrometers -- desirable -- the range of further 2-25 micrometers -- furthermore, 2-15 micrometers is still more alike, and the range of 2-9 micrometers is desirable It becomes difficult in below this range to handle [ of a particle ] a volume mean diameter, and it is not practical as an additive for paints etc. above this range. As for the particle size distribution of the particle of this invention, it is desirable for the particle of the range of particle diameters  $0.5D$ - $2.0D$  to occupy more than 70wt% of the whole, and, as for more than 80wt% and a further, it is preferably desirable to occupy more than 85wt% and also more than 90wt%. moreover, the particle-diameter range which more than 70wt% occupies according to another expression -- the range of  $0.6D$ - $1.8D$  -- desirable -- further -- the range of  $0.7D$ - $1.5D$  -- furthermore, the range of  $0.8D$ - $1.3D$  -- still more -- being alike -- it is desirable that it is the range of  $0.9D$ - $1.2D$  Moreover, as for the coefficient of variation which is the value which \*(ed) standard deviation by the average, it is desirable that it is 30% or less, and it is preferably desirable that they are 15% or less and also 10% or less still more preferably 20% or less.

[0007] It has an independent hole single [ the particle of this invention ] inside a particle, or multiple. In the case of which [ the ], in this invention, it makes it indispensable to be the range whose void content is 1 - 99vol%. here -- a void content -- a particle -- inner -- a hole -- it is the value which \*(ed) capacity by the appearance volume of a particle a void content -- the range of 2 - 98vol% -- desirable -- further 5 - 95vol% -- furthermore, the range of 10 - 95vol% -- still more -- being alike -- the range of 20 - 90vol% is desirable It is filled with the gas or the liquid, and this hole has air, nitrogen, 2 desirable carbon monoxide, etc. as a gas, and is desirable as a liquid. [ of water ] although especially the particle of this invention does not limit this, when it dries, the ranges of apparent specific gravity when a hole is filled with a gas are 0.1-1.3 -- desirable -- further -- the range of 0.2-1.2 -- furthermore, the range of 0.5-1.0 is desirable

[0008] The particle of this invention makes polyester resin a principal component. polyester resin -- the use beyond 50wt% of all resinous principles -- indispensable -- more than 80wt% -- desirable -- further - - more than 90wt% and also more than 95wt% -- still more -- alike -- more than 98wt% -- containing is desirable It becomes polyester resin in this invention from multiple-valued carboxylic acids and polyhydric alcohol. As multiple-valued carboxylic acids used for polyester resin For example, - terephthalic acid, an isophthalic acid, an orthochromatic phthalic acid, 1, 5-naphtha RUREN dicarboxylic acid, 2, 6-naphthalene dicarboxylic acid, 9, 10-anthracene dicarboxylic acid, 9, 10-

anthracene dipropionic acid, diphenic acid, a sulfo terephthalic acid, 5-sulfoisophtharic acid, 4-sulfo phthalic acid, 4-sulfo naphthalene-2,7-dicarboxylic acids, 5 [4-sulfo phenoxy] isophthalic acids and a sulfo terephthalic acid -- and -- or those metal salts -- Aromatic dicarboxylic acids, such as an ammonium salt, a p-oxy-benzoic acid, Aromatic hydroxy acids, such as p-(hydroxy ethoxy) benzoic acid, - Aliphatic dicarboxylic acids, such as a succinic acid, an adipic acid, an azelaic acid, a sebacic acid, and a dodecane dicarboxylic acid, - A fumaric acid, a maleic acid, an itaconic acid, a mesaconic acid, a citraconic acid, An aromatic unsaturation multiple-valued carboxylic acid and hexahydrophthalic acid, such as an aliphatic unsaturation multiple-valued carboxylic acid of \*\*, and - phenylene diacrylic acid, The multiple-valued carboxylic acid more than trivalence, such as alicycle group dicarboxylic acids, such as a tetrahydrophthalic acid, - trimellitic acid, a trimesic acid, and pyromellitic acid, etc. can be illustrated.

[0009] In this invention, you may use monocarboxylic acids together in part to multiple-valued carboxylic acids. As monocarboxylic acids, aromatic monocarboxylic acids are desirable. As an aromatic monocarboxylic acid, for example, a benzoic acid, a chloro benzoic acid, A BUROMO benzoic acid, the Para hydroxybenzoic acid, a naphthalene carboxylic acid, 4-methyl benzoic acid, 3 methyl benzoic acid, a salicylic acid, a thiosalicylic acid, Phenylacetic acids and these low-grade alkyl ester, a sulfobenzonic acid monochrome ammonium salt, A sulfobenzonic acid monosodium salt, a cyclohexyl aminocarbonyl benzoic acid, It is more desirable especially to be able to use n-dodecylamino carbonyl benzoic acid, a TA-SHARU butyl benzoic acid, a naphthalene carboxylic acid, an anthracene carboxylic acid, a TA-SHARU butyl naphthalene carboxylic acid, etc., and to use a TA-SHARU butyl benzoic acid. The amount of this aromatic monocarboxylic acid used has more desirable 2-25-mol % and further 5-20-mol% of use to an acid component. [ % and also 8-16 mol % ] In this invention, the unsaturation aliphatic multiple-valued carboxylic acid beyond 5mol% of this multiple-valued carboxylic-acid component can be used. As an unsaturation multiple-valued carboxylic acid in this invention, use of a fumaric acid and a maleic acid is desirable, and use of a fumaric acid is still more desirable. More than 5mol% of use of an unsaturation multiple-valued carboxylic acid is indispensable to an acid component, it is desirable, and is still more desirable. [ 30-50 mol% of ] [ 20-50 mol% of ]

[0010] As polyhydric alcohol used for polyester resin, aliphatic polyhydric alcohol, alicycle group polyhydric alcohol, and aromatic polyhydric alcohol can be illustrated.

As aliphatic polyhydric alcohol, - Ethylene glycol, a propylene glycol, 1,3-propanediol, 2,3-butanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexandiol, neopentyl glycol, A diethylene glycol, a dipropylene glycol, 2 and 2,4-trimethyl-1,3-pentanediol, Triol, such as aliphatic diols, such as a polyethylene glycol, a polypropylene glycol, and a polytetramethylene glycol, trimethylolpropane, a glycerol, and pen TAERUSURITO-RU, and TETORAO-RU can be illustrated.

[0011] - As alicycle group polyhydric alcohol, the ethyleneoxide addition product of 1,4-cyclohexandiol, 1,4-cyclohexane dimethanol, SUPIROGURIKO-RU, hydrogenation bisphenol A, and hydrogenation bisphenol A and a propylene oxide addition product, a tricyclodecane diol, tricyclodecane dimethano-RU, etc. can be illustrated.

- As aromatic polyhydric alcohol, an ethyleneoxide addition product, a propylene oxide addition product, etc. of a paraxylene glycol, a meta key sea lane glycol, an ortho xylene glycol, 1,4-phenylene glycol, 1, the ethyleneoxide addition product of 4-phenylene glycol, bisphenol A, and bisphenol A can be illustrated.

- Lactone system polyester poliomyelitis-RU obtained by carrying out ring opening polymerization of the lactone, such as epsilon-caprolactone, can be further illustrated as polyester poliomyelitis-RU.

- Monoalcohol, such as fatty alcohol, an aromatic alcohol, and alicycle group alcohol, can be used like carboxylic acids again.

[0012] The glass transition point of the polyester resin in this invention has desirable 40 degrees C or more, and 45 degrees C or more 50 degrees C or more are 70 degrees C or more preferably [ it is still more desirable and ] to 60 degrees C or more and a pan preferably. When a glass transition point is lower than this, it may become difficult for the inclination blocked during handling or preservation to handle the fine particles seen and obtained. The number average molecular weight of the polyester resin

of this invention has the desirable range of 1000-20000. Moreover, or more 2000 5000 or less range is desirable, and or more 3000 4000 or less range is still more desirable.

[0013] It is indispensable to contain an ionicity machine in polyester resin in the range of 20-2000eq./ton in this invention. As an ionicity machine, it is cation nature machines, such as anionic machines, such as a sulfonic group, a carboxyl group, a sulfuric-acid machine, a phosphoric-acid machine, a phosphonic acid machine, phosphinic acid machines or those ammonium salts, and a metal salt, the 1st class, or a tertiary amine machine, and the basis of a sulfonic-acid alkali-metal salt and a carboxylic-acid ammonium-salt machine can be used preferably. As for these ionicity machine, it is desirable to contain with the gestalt by which copolymerization was carried out to polyester, or the gestalt introduced into the macromolecule end. as the sulfonic-acid metal base content multiple-valued carboxylic acid which can be copolymerized in polyester -- a sulfo terephthalic acid, 5-sulfoisophtharate, 4-sulfo phthalic acid, 4-sulfo naphthalene -2, 7 dicarboxylic acids, and 5 [4-sulfo phenoxy] isophthalic acids -- and -- or those salts can be illustrated Moreover, a sulfonic-acid metal base can be introduced into a macromolecule end by using the metal salt of sulfobenzonic acid together. As a salt, they are ammonium system ion, and Li, Na, K, Mg, calcium, Cu, Fe and nickel. Salts, such as Co and aluminum, are raised and especially a desirable thing is K salt or Na salt.

[0014] A carboxyl group can be added to a macromolecule end by introducing multiple-valued carboxylic acids, such as trimellitic acid, in a system in the polymerization last stage of polyester. It is exchangeable for the basis of a carboxylate by furthermore neutralizing this in ammonia, a sodium hydroxide, etc. the content of these ionicity machine -- this polyester resin -- receiving -- the range of 20-2000eq./ton -- indispensable -- desirable -- 20 - 500eq./ton and a pan -- desirable -- 50-200eq./ton -- it is . The above is the indispensable requirements by which the hollow polyester resin particle of this invention is characterized.

[0015] The concrete method for obtaining the polyester resin particle of this invention is described below. It is the method of hollow-izing simultaneously with formation of - polyester particle as a method of obtaining the hollow polyester resin particle of this invention.

- How to hollow-ize a solid polyester particle by after treatment.

It can divide roughly into two sorts of \*\*.

[0016] The method of dissolving 1 ionicity machine content polyester resin in a water-soluble organic compound, making W/O/W emulsion forming by subsequently adding water as the former, and obtaining an empty capsid can be illustrated. How to heat-treat the solid particle of 2 ionicity machine content polyester resin in a drainage system medium as the latter more than a glass transition temperature, 3) How to hollow-ize, in case azeotropy removes this water-soluble organic compound, after adding a water-soluble organic compound to the drainage system dispersing element of an ionicity machine content polyester resin particle, 4) A solvent is added to the drainage system dispersing element of an ionicity machine content polyester resin particle, and after making a particle swell, in case it is made to dry by methods, such as spray dry, the method of hollow-izing etc. can be illustrated. Although the resin particle obtained by carrying out trituration classification of the ionicity machine content polyester resin as a faithful polyester particle used in the method of the latters 2-4 may be used, it is desirable to use the polyester resin particle obtained by the method described below preferably.

[0017] The ionicity machine content polyester resin in this invention has water-dispersion. The drainage system fine dispersing element of the ionicity machine content polyester resin of this invention can be manufactured by well-known arbitrary methods. That is, ionicity machine content polyester resin and a water-soluble organic compound are beforehand mixed at 50-200 degrees C, water is added to this, or the mixture of an ionicity machine content polyester system resin and a water-soluble organic compound is added to water, and it is manufactured by agitating at 40-120 degrees C. Or an ionicity machine content polyester system resin is added in the mixed solution of water and a water-soluble organic compound, and it is manufactured also by the method of agitating and distributing at 40-100 degrees C. As a water-soluble organic compound, ethanol, a butanol, an isopropanol, ethylcellosolve, a butyl cellosolve, a dioxane, a tetrahydrofuran, an acetone, a methyl ethyl ketone, etc. can be used. Especially use is not restricted although combined use is not desirable in a surfactant. Thus, the mean particle

diameter of the drainage system fine dispersing element obtained is about 0.01-1.0 micrometers in general. A polyester particle can be obtained by leading this differential granule-application child to a \*\*\*\*\* field, and carrying out particle growth by meanses, such as electrolytic addition, under the condition which this ionicity machine content polyester resin plasticizes to the drainage system fine dispersing element of this ionicity machine content polyester resin.

[0018] As an electrolyte used in this invention, the common inorganic or organic water-soluble salt represented by a sodium sulfate, an ammonium sulfate, potassium sulfate, magnesium sulfate, sodium phosphate, phosphoric acid 2 hydrogen sodium, phosphoric acid hydrogen disodium, an ammonium chloride, a calcium chloride, a cobalt chloride, a strontium chloride, a cesium chloride, barium chloride, a nickel chloride, a magnesium chloride, a rubidium chloride, a sodium chloride, potassium chloride, sodium acetate, an ammonium acetate, potassium acetate, the sodium benzoate, etc. can be used. The concentration of these electrolytes has the desirable range of 0.01 - 2.0 mol/l, further 0.1 - 1.0 mol/l, and also 0.2 - 0.8 mol/l, when using a univalent electrolyte. When using the electrolyte of a multiple valued furthermore, the addition is good in a fewer amount. In this invention, although it is possible to fully attain the purpose by preparing the aforementioned electrolyte beforehand in a system, or back-adding, a still better polyester resin particle can be obtained by what "is electrolyte-ized after adding an electrolyte precursor" preferably.

[0019] The compound disassembled and electrolyte-ized [ an elevated temperature and ] by poor solubility, a soluble salt, pH, temperature, the pressure, optical irradiation, etc. at low temperature as an electrolyte precursor can be illustrated. In this invention, the ester compounds of amino alcohols and carboxylic acids can be used as a desirable electrolyte precursor. Since this ester compound has an amino group, water solubility is shown, and the solution shows alkalinity. When the temperature up of this alkaline-water solution is carried out, ester combination is understood an added water part and serves as a salt with amino alcohols and a carboxylic acid. The amino group functions as a first-class ammonium or the 3rd class ammonium in fact. In this invention, amino ethanol, 1, 3-amino propanol, 1, a 4-amino butanol, dimethylamino ethanol, 1, 3-dimethylamino propanol, diethylamino ethanol, diethylamino propanol, etc. can be used as desirable amino alcohols. As carboxylic acids, a benzoic acid and its derivative, a naphthalene carboxylic acid and its derivative, a salicylic acid, a thiosalicylic acid, a phenylacetic acid, an acetic acid, a propionic acid, butanoic acid, an octanoic acid, a decanoic acid, dodecanoic acid, a lauryl acid, a stearyl acid, an acrylic acid, a methacrylic acid, etc. can be used. Furthermore in this invention, the ester of the arbitrary combination of these amino alcohols and carboxylic acids can be preferably used as an electrolyte precursor.

[0020] Thus, the obtained polyester particle is a real globular form, and has a sharp particle size distribution, and elevated-temperature distribution dyeing is possible for it to high concentration. as for a particle size distribution, the particle of the range of particle diameters 0.5D-2.0D occupies 80% of the weight or more of the whole by the ability of the polyester particle obtained in this way controlling the volume mean particle diameter D in 1-100 micrometers freely (based on electrolyte concentration, temperature, and time), and coefficient of variation becomes 30% or less of sharp thing, and calls it 0.8 or more average sphericity (a minor axis/major axis) -- it becomes a globular form polyester particle substantially

[0021] The singularity of the particle of this invention to the particle of the vinyl system polymer obtained according to a suspension polymerization etc. is demonstrated by not only the versatility of the physical properties of polyester resin but the configuration of such a polyester particle and a particle size distribution. A particle size distribution is broadcloth and, especially as for a general suspension-polymerization particle, only the thing of about 30% or more of coefficient of variation is obtained. this invention -- adjustment of particle-ized conditions -- the particle of the range of particle diameters 0.5D-2.0D -- 80% of the weight or more of the whole -- desirable -- 85 % of the weight or more -- further -- desirable -- 90 % of the weight or more -- furthermore, 95% of the weight or more of a thing can be obtained preferably Moreover, coefficient of variation can be preferably made into 10% or less preferably [ it is still more desirable and ] to 15% or less and a pan 20% or less 30% or less. Moreover, it can take still still more preferably or more for 0.95 0.9 or more still more preferably 0.85 or more

preferably 0.8 or more average sphericity (a minor axis/major axis). In addition, the value which <sup>\*\*</sup>(ed) standard deviation by the average is called coefficient of variation here.

[0022] As the obtained polyester resin particle was mentioned above, in thus, the state where it distributed to the drainage system medium - How to hollow-ize, in case azeotropy removes this water-soluble organic compound, after adding the method and - water-soluble organic compound which are heat-treated more than a glass transition temperature, - Add a solvent, and after making a particle swell, in case it is made to dry by methods, such as spray dry, obtain a predetermined empty capsid by carrying out on methods, such as the method of hollow-izing. It is most desirable to use the method of heat-treating in this invention more than - glass transition temperature, and according to this method, a percentage of hollowness of fibre is arbitrarily controllable by the temperature of heat-treatment, and the nature concentration of electric field in a system. As processing temperature, the temperature of a before [ from the glass transition temperature of polyester resin / 200 degrees C ] is desirable, and 90 degrees C or less are [ the temperature of 140 degrees C or less is still more desirable, 100 degrees C or less are still more desirable, and ] still more desirable. Electrolyte concentration has the desirable range of 0.2 or less mol/l, its 0.1 or less mol/l is in addition desirable, and its 0.05 or less mol/l is still more desirable.

[0023] To the polyester resin particle of this invention, a water dispersing element of a different kind can be incorporated by hetero condensation in a particle growth process. Moreover, it can also be with the polyester fine dispersing element colored with the color etc. Thus, coloring and functionalization of a particle are possible. Water dispersing elements of a different kind are dispersing elements, such as a pigment, a latex, and carbon black. The obtained particle is taken out by meanses, such as freeze drying, spray drying, fluidized drying, and a vacuum drying, as dryness fine particles after washing dehydration. It is used still in the state in the state where it distributed to the drainage system medium depending on the use, of course.

[0024] Since it has a suitable hole for the interior, the hollow resin particle which makes a principal component the polyester resin obtained in this way has the high scattering effect of a beam of light, and when it uses as an additive for paints, it can direct advanced white nature. Moreover, high adiathermancy is expectable with the heat insulation effect of an internal hole. When a gas is filled to the hole inside a further, since apparent specific gravity is small, it is advantageous to lightweight-izing. Moreover, by the same reason, since apparent specific inductive capacity is small, it is useful also as a low dielectric material. Moreover, when it has an unsaturation double bond in polyester resin, it is possible to improve thermal resistance and solvent resistance by meanses, such as bridge formation. Although these operations are also expected to the hollow resin particle of the vinyl system polymer known conventionally, they can acquire the effect which was excellent when the adhesive property to the high polyester film of versatility was excellent in matching with a high polyester system binder and blended with this binder, since polyester resin was further used for the main constituent in this invention.

[0025] Although an example is shown below and this invention is further explained to a detail, this invention is not the object limited to these in any way.

[Example]

[Polyester resin (A1) - (A3), the polymerization of (A6)]

To the inside of the autoclave equipped with the thermometer and the agitator Dimethyl-terephthalate ester 80 Weight section Isophthalic-acid dimethyl ester 80 Weight section 5-sodium sulfoisophtharate dimethyl ester 6 Weight section Ethylene glycol 68 Weight section Neopentyl glycol 114 the weight section -- and -- Tetrabutoxy titanate 0.1 the weight section -- teaching -- 120-220 degrees C -- for 120 minutes -- heating . The ester exchange reaction was performed. Subsequently, the temperature of the system of reaction is lowered to 180 degrees C. Fumaric acid 20 Weight section Hydroquinone 0.1 As a result of having added the weight section, having continued the reaction for 60 minutes at 200 degrees C, raising the temperature of the system of reaction to 220-240 degrees C and continuing a reaction for 60 minutes as a system pressure 1 - 10mmHg after that, the copolymerized polyester resin (A1) was obtained. Composition of the obtained copolymerized polyester resin (A1), a glass transition temperature, the acid number, molecular weight, and the sulfonic-acid sodium machine equivalent are



shown in table 1. GPC and the sulfonic-acid sodium machine equivalent searched for for DSC and the acid number with titration, and molecular weight searched for [ NMR analysis and the glass transition temperature ] composition of polyester by the fixed quantity of S. Hereafter, the raw material was changed, the polymerization was performed similarly, and polyester resin (A2) - (A3) shown in table 1. was obtained.

[0026]

[Table 1]

ポリエステル樹脂		実施例					比較例
		A 1	A 2	A 3	A 4	A 5	A 6
多価 カルボン酸	NDC	—	40	—	—	—	—
	TPA	40	29	49	65	—	50
	IPA	40	29	48	30	—	50
	FA	18	—	—	—	—	—
	MA	—	—	—	—	100	—
	SIP	2	2	3	1	—	—
	TMA	—	—	—	4	—	—
多価アルコール	EG	50	30	40	50	—	50
	NPG	50	70	—	50	—	50
	BPP	—	—	60	—	100	—
T <sub>g</sub> [°C]		45	79	67	59	54	58
数平均分子量		3000	2800	2700	3100	2200	3000
重量平均分子量		4500	4300	3700	5300	3500	4500
酸価 [mgKOH]		0.1	0.1	0.1	3.2	16.5	0.0
S当量 [eq./ton]		110	98	125	45	0	0

[The polymerization of polyester resin (A4)]

To the inside of the autoclave equipped with the thermometer and the agitator Dimethyl terephthalate 128 Weight section Ethylene glycol 45 Weight section Propylene oxide addition product of bisphenol A 270 Weight section Tetrabutoxy titanate 0.1 The weight section is taught and it heats for 180 minutes at 150-220 degrees C. The ester exchange reaction was performed. Subsequently, the temperature of the system of reaction is lowered to 180 degrees C. Maleic anhydride 29 Weight section Hydroquinone 0.1 30 minutes after having added the weight section, continuing the reaction for 60 minutes at 200 degrees C, carrying out the temperature up of the temperature of the system of reaction to 220-240 degrees C after that and reducing a system pressure gradually, it was referred to as 10mmHg(s), and the reaction was continued for 60 minutes. Nitrogen gas replaced the inside of an autoclave after that, and it considered as atmospheric pressure. Temperature was kept at 200 degrees C, 8 weight sections were added for trimellitic anhydride, the reaction was performed for 60 minutes, and the copolymerized polyester resin (A5) shown in table 1. was obtained.

The propylene oxide addition product 700 weight section of bisphenol A, the maleic-anhydride 196 weight section, and the hydroquinone 1 weight section were taught into the autoclave equipped with the [polymerization of polyester resin (A5)] thermometer, and the agitator, and nitrogen gas was introduced in the system of reaction, it maintained at the inert atmosphere, and the polyester resin (A5) which adds the dibutyl tin oxide of the 0.05 weight sections, is made to react at 200 degrees, and is shown in table 1. was obtained.

[0027] In addition, for neopentyl glycol BPP, propylene oxide addition product (average molecular weight 350) Tg of bisphenol A is [ NDCin table 1. / ethylene glycol NPG ] glass transition temperature. 1, 5-naphthalene dicarboxylic acid TPA Terephthalic-acid IPA Isophthalic-acid SIP 5-sodium sulfoisophtharate FA Fumaric-acid MA Maleic acid TMA Trimellitic acid EG It is shown.

[0028] After adding the water 680 80-degree C section after dissolving the [manufacture of polyester



drainage system fine dispersing element] polyester resin (A1) 300 weight section, the methyl-ethyl-ketone 150 weight section, and the tetrahydrofuran 140 weight section at 80 degrees C, and considering as the drainage system fine dispersing element of the copolymerized polyester resin of about 0.1 micrometers of particle diameters, until it puts into the flask for distillation and fraction temperature amounts to 100 degrees C. It distilled and the polyester drainage system differential granule-application child (B1) of 30% of solid-content concentration by which added water and desolventization was carried out after cooling was obtained. (B-2) and (B3) were obtained from polyester resin (A2) and (A3) by the same method as the following, respectively. After adding the butanol 100 section to the polyester (A4) 300 section and dissolving in it at 90 degrees C, it cooled to 80 degrees C. After having added the 1-N aqueous ammonia solution so that it might furthermore become the acid number of copolymerized polyester with equivalence, holding 80 degrees C and agitating for 30 minutes, the water 500 80-degree C section was added, and the drainage system fine dispersing element of copolymerized polyester was obtained. Water differential \*\*\*\* furthermore obtained was put into the flask for distillation, after distilling until it reached the fraction temperature of 100 degrees C, it cooled, and water differential \*\*\*\* (B4) of copolymerized polyester of 30% of solid-content concentration by which desolventization was finally carried out was obtained. The fine dispersing element (B5) was obtained from polyester resin (A5) by the same method as the following. Although same operation was performed using resin polyester (A6), a fine dispersing element was not able to be obtained.

[0029] [-- manufacture [ of a polyester particle ]: -- a wet agglomeration method -- the polyester drainage system fine dispersing element (B1) 300 weight section was taught to] thermometer, the capacitor, and the 1l. separable flask of the 4 mouths equipped with the impeller, and the temperature up was carried out to 80 degrees C. Subsequently, churning was continued, where it added over for 60 minutes (0.2 mol/l) and the 20 % of the weight solution 40 weight section of dimethylaminoethyl methacrylate is kept at 80 degrees C for 300 more minutes. The conductivity in a system descended to 25mS(s) from about 1 mS, and elevation and pH descended even to 6.7 from 10.8. Understanding the added dimethylaminoethyl methacrylate an added water part to back completeness mostly, and having become the salt of dimethylamino ethanol and a methacrylic acid from this was checked. The copolymer of the particle diameter of sub MIKURONO-DA - which existed in the polyester drainage system micro dispersing element carried out coalesce particle growth with time, and obtained the polyester spherical particle (C1) shown in table 2. In addition, a mean particle diameter, a particle size distribution, and coefficient of variation were measured among table 2. using Coulter counter TA 2. Moreover, sphericity was measured by processing the scanning-electron-microscope photograph of a particle with the image processing system image analyzer V1 [the Toyobo Co., Ltd. make]. Front Naka DAM shows dimethylaminoethyl methacrylate. It experimented by having changed a raw material and conditions like the following, and polyester particle (C2) - (C6) shown in table 2. was obtained.

[0030]

[Table 2]

粒子製法	湿式造粒法						粉碎法	
ポリエステル粒子	C 1	C 2	C 3	C 4	C 5	C 6	C 7	C 8
ポリエステル樹脂	A 1	A 2	A 3	A 4	A 5	A 2	A 3	A 6
DAM濃度[mol/l]	0.20	0.20	0.20	0.20	0.20	0.12	—	—
平均粒径D [μm]	7.8	3.2	4.4	6.5	6.2	1.8	10.5	10.7
0.5D-2D 占有率[%]	98	97	99	98	99	99	78	75
変動係数 [%]	8.9	10.2	8.6	11.3	9.4	7.5	25.4	26.8
真球度	0.99	0.98	0.99	0.97	0.98	0.98	0.68	0.70

[-- manufacture [ of a polyester particle ]: -- the grinding method -- after carrying out coarse grinding of the] polyester resin (A3) with a chopper-mill -- supersonic jet mill PJM200 type -- pulverizing -- pulverization \*\*\*\*\* -- carrying out (C7) -- it obtained The pulverization particle (C8) was similarly obtained from polyester resin (A6).

[0031] After carrying out dehydration washing of the [creation of empty capsid] polyester particle (C1) and re-distributing in water, it considered as the polyester particle water dispersing element which diluted with deionized water and adjusted solid-content concentration to 5%. It cooled by raising the temperature of a system to 90 degrees C, and pouring out the deionized water 2000 weight section after 30 minutes, having taught the 1000 weight sections to the separable flask and agitating a polyester water dispersing element calmly. In suction ROUTO, dehydration washing was carried out, the vacuum drying of the obtained particle was carried out, and the hollow polyester particle (D1) was obtained. The mean particle diameter of the obtained particle, a particle size distribution, coefficient of variation, sphericity, apparent specific gravity, and a void content are shown in table 3. It asked for the void content from the density difference of a particle. Polyester particle (C2) - (C7) to empty capsid (D2) - (D7) was obtained like the following. When a polyester particle (C8) was used, the particle condensed in the middle of the temperature up, and an empty capsid was not able to be obtained.

[0032]

[Table 3]

中空粒子	D 1	D 2	D 3	D 4	D 5	D 6	D 7	—
ポリエステル粒子	C 1	C 2	C 3	C 4	C 5	C 6	C 7	C 8
ポリエステル樹脂	A 1	A 2	A 3	A 4	A 5	A 2	A 3	A 6
電解質濃度 [mol/l]	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
処理温度 [°C]	90	90	90	90	90	90	90	90
平均粒径D [ $\mu$ m]	13.3	5.4	7.5	11.1	10.4	3.0	18.5	凝集
0.5D-2D 占有率[%]	98	96	98	98	98	99	76	
変動係数 [%]	9.2	9.6	10.4	10.5	9.7	8.7	24.5	
真球度	0.99	1.00	0.99	0.99	1.00	1.00	0.99	
見かけ比重	0.26	0.25	0.26	0.27	0.26	0.28	0.25	
空孔率 [%]	81.5	82.4	79.5	78.4	80.2	81.5	82.3	

As the water dispersing element 1000 weight section of a polyester particle (C3) which adjusted [control of void content] solid-content concentration to 2%, and an electrolyte. 0.58g (an equivalent for 0.01 mol/l) of sodium chlorides was taught to the stainless steel pot of a dyeing test machine mini color [made in TEKUSAMU Research Institute], in suction ROUTO, dehydration washing was carried out, the vacuum drying of the particle which processed for 30 minutes and was obtained after water cooling at 90 degrees C was carried out, and the hollow polyester particle and the empty capsid (D9) shown in table 4. were obtained. It experimented by having changed temperature and electrolyte concentration like the following, and hollow polyester particle (D10) - (D16) was obtained. That is, it was shown by this invention with the electrolysis room concentration of a processor, and processing temperature that control of a void content is possible.

[0033]

[Table 4]

中空粒子	D 9	D10	D11	D12	D13	D14	D15	D16
ポリエステル粒子	C 3	C 3	C 3	C 3	C 3	C 3	C 3	C 3
ポリエステル樹脂	A 3	A 3	A 3	A 3	A 3	A 3	A 3	A 3
電解質濃度 [mol/l]	0.01	0.02	0.05	0.10	0.15	0.0	0.0	0.0
処理温度 [°C]	90	90	90	90	90	75	100	130
平均粒径 D [ $\mu$ m]	6.8	5.4	5.0	4.8	4.6	4.6	8.0	12.6
0.5D-2D 占有率[%]	98	99	99	99	99	99	99	99
変動係数 [%]	10.5	10.2	9.6	9.8	10.0	9.9	9.7	9.6
真球度	1.00	0.99	1.00	0.99	1.00	1.00	1.00	0.99
見かけ比重	0.34	0.70	0.89	1.05	1.15	1.16	0.21	0.06
空孔率 [%]	75.2	48.2	30.4	20.1	10.2	9.8	86.7	95.6

As the water dispersing element 1000 weight section of a polyester particle (C3) which adjusted [low-specific-gravity and low dielectric constant Plastic-solid] solid-content concentration to 2%, and an electrolyte. The polyester empty capsid with which 1.16g (an equivalent for 0.02 mol/l) of sodium chlorides was taught to the stainless steel pot of a dyeing test machine mini color [made in TEKUSAMU Research Institute], dehydration washing of the particle which processed for 30 minutes and was obtained after water cooling at 90 degrees C was carried out in suction ROUTO, and water was filled by the hole was obtained. The water content of the dehydration cake of the obtained polyester empty capsid was 76%.

[0034] The water dispersing element (B1) obtained from polyester resin (A1) was used as a drainage system binder. The styrene 20 weight section which dissolved the benzoyl peroxide 1 weight section in this binder 100 weight section was added, and it agitated at the room temperature for 30 minutes. Furthermore, the dehydration cake 500 weight section obtained previously was added, after mixing to this, slushing into the silicone rubber type and heating to it for 120 minutes at 70 degrees C, it cooled to it, and the vacuum drying was carried out to it, and the Plastic solid was obtained. The apparent specific gravity of the obtained Plastic solid was 0.68. When the specific inductive capacity of the Plastic solid obtained by the Q meter was measured, specific inductive capacity was 1.87.

[White polyester tailcoat film] The dehydration cake 50 weight section was added and agitated in the above-mentioned drainage system binder 200 weight section. The obtained dispersion liquid were applied in the bar coating machine on polyester film, and dryness hardening was carried out. the obtained film -- a whiteness degree -- excelling -- moreover, the adhesive property of a paint film -- the result of a squares cross-cut Scotch tape friction test -- 100/100 it was .

[0035]

[Effect of the Invention] As stated above, the polyester particle in this invention is a particle of the polyester resin which is condensed-system polymer, it has arbitrary particle diameters and arbitrary void contents, and are low specific gravity and a low dielectric constant, and is excellent in matching with a polyester system binder and a film.

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[Translation done.]

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(54) 【発明の名称】 小型高密度多心コネクタ

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【特許請求の範囲】

【請求項1】 平板状で長手方向にU形をなす2枚の導電板の先端に、板幅方向の一側に凹み、かつ互いの導電板を重ねると凹み同士が向合うようにした切欠部を設けて、2つの導電板を重ねることにより、一端に二又フォーク状の接触部を他端に接続部を備えたU形をなす接触子を形成し、その接触子多数を、各接触部同士が近接するとともに互いに平行をなすように、かつ各接続部同士が千鳥形に並ぶようにして、電気絶縁材よりなるケースに埋設してなる小型高密度多心コネクタ。

【発明の詳細な説明】

〔産業上の利用分野〕

本発明は、たとえばコンピュータや電子機器等に使用して効果的な、小型で高密度の多心コネクタに関するものである。

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〔従来の技術〕

第7図～第9図は、コンピュータや電子機器に使用される多心コネクタ(01)を示すもので、その接触子(02)は、形状が単純で偏平であるため、小型化と高密度化が容易であり、このようなコネクタ(01)に適している。接触子(02)は、たとえば接触抵抗が低くて、弾性の大きい銅合金板を、プレスにより打抜いたもので、中央部の導電部(03)の前端(図示左端)には、二又フォーク状の接触部(04)を形成する2本の接触片(05)(05)が設けられ、両接触片(05)(05)の間は接触溝(06)となっており、かつ導電部(03)の後端には接続部(07)が延設されている。

コネクタ(01)は、多数の接触子(02)を平行にかつ近接して並べるとともに、各導電部(03)を、合成樹脂製ケース(08)内に埋設し、かつケース(08)の前端に、

前面より、各接触部(04)を囲む有底の嵌合孔(09)と案内溝(010)を設け、後面より突出する接続部(07)に、リード線(図示省略)を半田付けするようになって

いる。  
(011)は、プリント配線基板の一部に設けた連結端子部、(012)は、上記各接触溝(06)に対応する帯状のプリントパターンによる導電片である。

連結端子部(011)に、コネクタ(01)の嵌合孔(09)を、案内溝(010)の案内により外嵌すれば、各接触子(02)の接触片(05)(05)は、互に離間する方向に若干弾性屈撓し、拡開する接触溝(06)に連結端子部(011)が突入し、両接触片(05)(05)は対応する導電片(012)と接触子(02)は電気的に結合される。

〔発明が解決しようとする課題〕

近来、ますますコネクタ(01)の小型化と高密度化が要求されるようになり、そのためには、接触子(02)自体の寸法をさらに小型化するとともに、多数の接触子(02)の配列ピッチを小として、ケース(08)内に組込む必要がある。

しかし、二又フォーク状の接触部(04)は、両接触片(05)(05)の弾性屈撓しうる範囲が本来狭いので、接触片(05)の寸法を小さくして、高密度化すると、弾性屈撓しうる長さがさらに短くなって、コネクタ(01)の着脱に大きな力を要し、安全に着脱することが困難となる。軽く着脱しうるように、両接触片(05)(05)の間隔または連結端子部(011)の厚さを調節すれば、必要な接触圧を得ることができずに、接触不良を起こすことがあり、各接触片(05)をなるべく長くして、弾性屈撓しうる範囲を広くする必要がある。

また実装密度の高いコネクタが要求されるときには、接触端子部(011)の基板にも薄いフィルム基板が用いられるが、この際には、接触溝(06)の幅を、フィルム基板に依じて、狭くする必要がある。

しかし、接触片(05)の長さを長くし、接触溝(06)の幅を狭くして、接触溝(06)を細長くすると、接触子(02)をプレスにより打抜く際、接触溝(06)の押え代が狭幅となるとともに、接触溝(06)を打抜くポンチの強度が低下して、打抜きが困難となる。従って、接触溝(06)の狭幅化と接触子(02)の小型化には限界がある。

また高密度化のために、隣接する接触子(02)(02)の間隔を狭くすると、各接続部(07)へのリード線の半田付けが困難となるので、接触子(02)(02)をあまり近接させることはできない。

〔課題を解決するための手段〕

本発明によれば、平板状で長手方向にL形をなす2枚の導電板の先端に、板幅方向の一側に凹み、かつ互いの導電板を重ねると凹み同士が向合うようにした切欠部を設けて、2つの導電板を重ねることにより、一端に二又フォーク状の接触部を他端に接続部を備えたL型をなす

接触子を形成し、その接触子多数を、各接触部同士が近接するとともに互いに平行をなすように、かつ各接続部同士が千鳥形に並ぶようにして、電気絶縁材よりなるケースに埋設することにより、上記課題は解決される。

〔作用〕

本発明のコネクタ(1)の接触子(2)は、導電板(3)を素材よりプレスで打抜いて製作する際、狭幅の接触溝(7)を、その接触溝(7)と同形のポンチをもって形成する必要がないので、従来の接触子(02)よりも小型で、接触溝(7)の狭幅な接触子(2)を、容易に製作することができる。

また、交互に180度反転配置して、多数の接触子(2)の各接続部(8)が千鳥形に並び、かつ隣接する接続部(8)(8)が上下にずれて並んで離間しているため、隣接する接触子(2)(2)の間隔の限界を、従来のコネクタ(01)の約1/2としても、リード線を半田付けすることができ、コネクタ(1)を小型かつ高密度化することができる。

〔実施例〕

第1図～第4図は、本発明の一実施例を示すもので、本発明のコネクタ(1)の接触子(2)は、重合する2枚の導電板(3)(3)より形成されている。

接触子(2)の中央の導電部(4)はL形に屈折しており、導電部(4)の第2図における左端(以下、方向は第2図に関して言う。)における一方の導電板(3)の上縁と、他方の導電板(3)の下縁には、左方を向き、かつ互いに接触部分を対向する上下1対の接触片(5)(5)が延設されて、二又フォーク状の接触部(6)を形成している。

両接触片(5)(5)の間には、接触溝(7)が形成されている。

導電部(4)の右端は、両導電板(3)(3)が重合して、接続部(8)となっている。

換言すると、接触子(2)は、平板状で名が手方向に中央にL形をなす導電部(4)を備えた2枚の導電板(3)(3)の先端に、板幅方向の一側に凹み、かつ両導電板(3)を、互いに側面のL形を合わせて重ねると凹み同士が向合うようにした切欠部(5a)を設けて、2つの導電板(3)を重ねることにより、一端には、切欠部(5a)の対向部分を接触溝(7)とする二又フォーク状の接触部を、他端には、側面形L形の部分を隔て接続部(8)を備えたものとなっている。

第5図と第6図に示すように接触子(2)は、上記接触子(02)と同材質の薄板を、プレスで打抜いて、第2図に示す接触子(2)を接続部(8)の端辺(8a)(右端)を軸に、右方の平帯状に展開させた形状の帯板(9)を形成し、かつ両端に形成された接触片(5)(5)を、その基部において、帯板(9)の厚さの1/2だけ上方に段状に屈曲させるとともに、中央における端辺(8a)を折り目として二つ折りにしたものである。

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この接触子(2)は、帯板(9)を打抜く際、接触溝(7)を形成する必要がないので、従来の接触子(02)より小型で、接触溝が狭幅のもの、たとえば、接触片(5)の厚さが0.2、最大幅が0.3、接触溝(7)の最小幅が0.2、接触片(5)の長さが3の接触子(2)を、容易に製作することができる。

上述のような多数の接触子(2)を、従来のコネクタ(01)の接触子(02)の標準ピッチ(2.54)の1/2として、各接触部(6)同士が近接して互に平行をなすように、かつ交互に接続部(8)を180度反転させ、各接続部(8)が千鳥形に並ぶように、上記コネクタ(10)と同様にケース(10)に組込めば、図示するような小型で高密度、たとえば同列に隣接する接触子(2)(2)の間隔が標準ピッチ2.54のコネクタ(1)が得られる。

なお、第1図と第2図における(11)と(12)は、それぞれ上記(09)と(010)に相当する嵌合孔と案内溝、(13)と(14)はそれぞれ上記(011)と(012)に相当する連結端子部と導電板である。

#### 〔発明の効果〕

本発明のコネクタ(1)の接触子(2)は、従来のコネクタ(01)の接触子(02)より小型で、接触溝(7)における狭幅の接触子(2)を容易に製作することができる。

また、多数の接触子(2)の接続部(8)が千鳥形に並んで、隣接する両接続部(8)(8)が上下に離間しているため、隣接する接触子(2)(2)の間隔を、従来のコネクタ(01)は著しく狭くしても、リード線を容易に半田付けすることができ、コネクタ(1)をより小型

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かつ高密度化することができる。

#### 【図面の簡単な説明】

第1図は、本発明のコネクタの一例を示す一部切欠平面図、

第2図は、第1図のII-II縦断側面図、

第3図は、本発明のコネクタの正面図、

第4図は、同じく背面図、

第5図は、本発明のコネクタの接触子の展開図、

第6図は、同じく平面図、

第7図は、従来のコネクタの一部切欠平面図、

第8図は、第7図のVII-VII縦断側面図、

第9図は、従来のコネクタの背面図である。

(1)……コネクタ

(2)……接触子

(3)……導電板

(4)……導電部

(5)……接触片

(5a)……切欠部

(6)……接触部

(7)……接触溝

(8)……接続部

(8a)……端辺

(9)……帯板

(10)……ケース

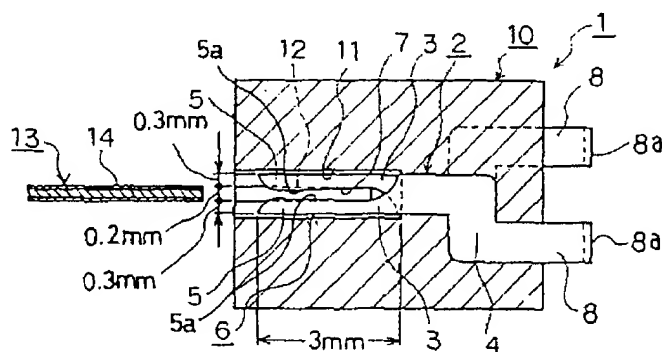
(11)……嵌合孔

(12)……案内溝

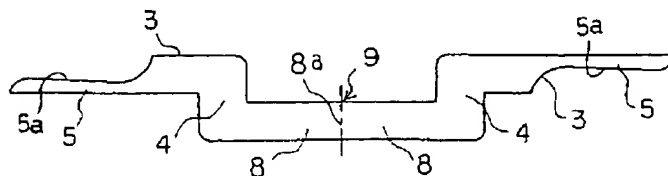
(13)……連結端子部

(14)……導電板

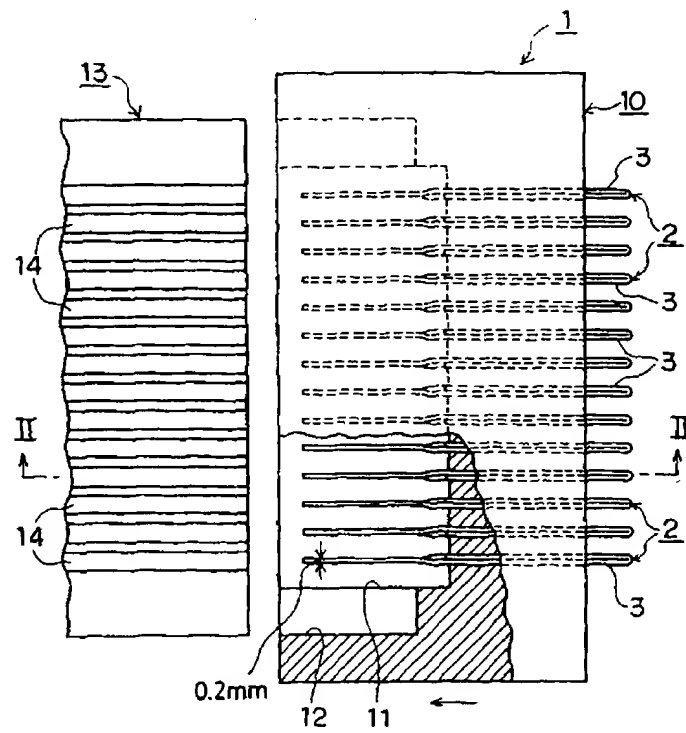
【第2図】



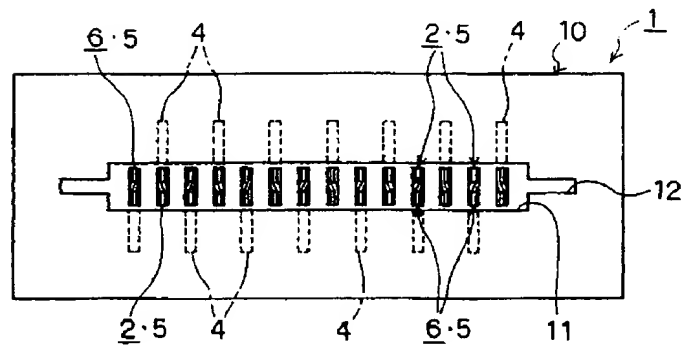
【第5図】



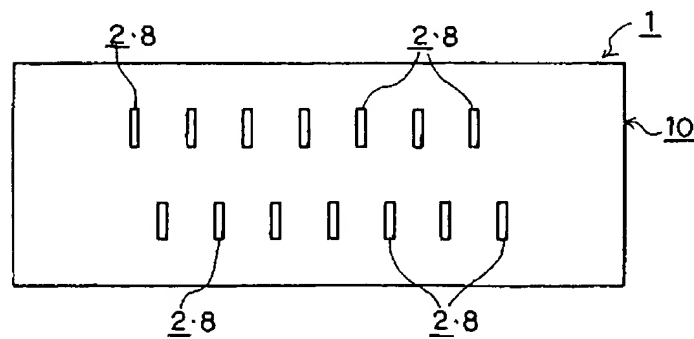
【第1図】



【第3図】

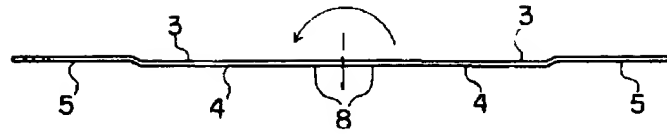


【第4図】

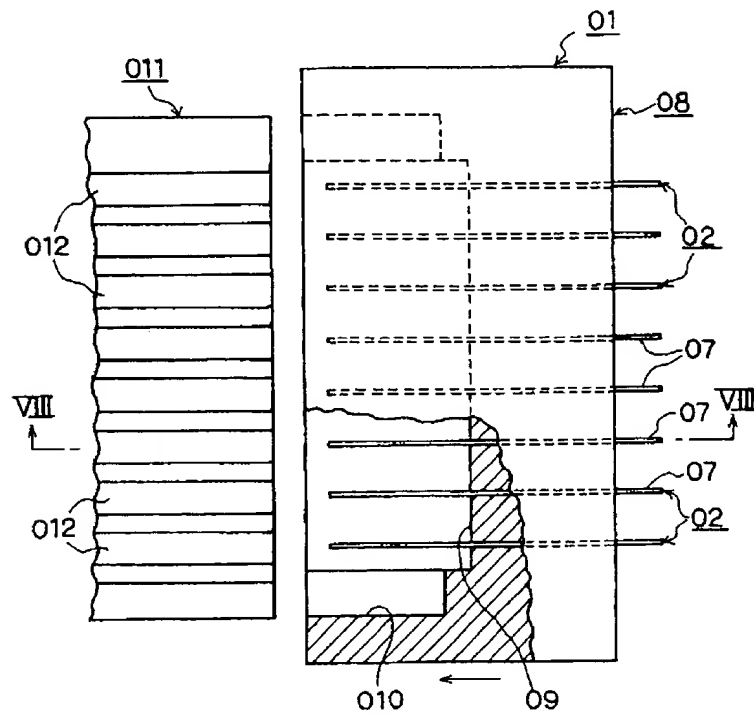




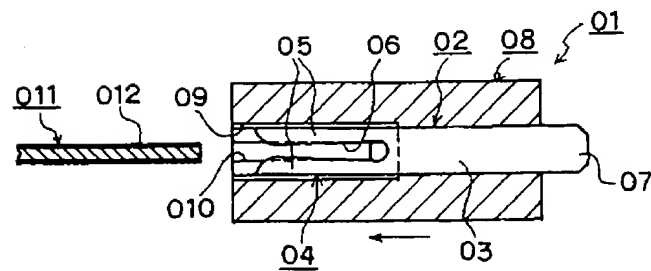
【第6図】



【第7図】



【第8図】



(6)

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【第9図】

